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# LOW ENERGY CHLORATE ELECTROLYTIC CELL AND PROCESS

## BACKGROUND OF THE INVENTION

### (1) FIELD OF THE INVENTION

This invention relates to an electrolytic cell, a low transport efficiency alkali metal ion permselective membrane, and a cyclic electrolysis process for the preparation of an alkali metal chlorate in an aqueous medium from the corresponding alkali metal chloride.

### (2) DESCRIPTION OF RELATED ART

It is known in this art to form sodium chlorate by the electrolysis of sodium chloride using a sodium chlorate electrolyte which is a mixture of sodium chloride and sodium chlorate at concentrations close to the saturation point. In the prior art commercial process, an electrolytic cell is used in which the anode and cathode are exposed to the same electrolyte; the cell not being divided into cathode and anode

compartments by a porous barrier, diaphragm, or membrane. At the anode in such a cell, chlorine is evolved and at the cathode, hydrogen is evolved. ~~Hydrogen produced at the cathode and~~ ~~c~~Chlorine produced at the anode combine in the prior art cell with the hydroxyl ions also produced at the cathode to form hypochlorite. As the electrolysis proceeds, the concentration of hypochlorite increases to a level at which some of the hypochlorite converts to chlorate. In order to limit the cathodic reduction of hypochlorite and/or chlorate ions, it is the practice in the prior art to carry out the electrolysis in the presence of hexavalent chromium values. The use of hexavalent chromium in the electrolyte is disadvantageous economically as well as environmentally, as set forth in U.S. patent No. 5,104,499 to Millet and U.S. patent No. 4,295,951 to Bommaraju et al. The anodes of the prior art chlorate cell are made from precious metal oxides, such as ruthenium, platinum, and iridium oxides which are deposited on a titanium substrate. The cathodes of the prior art chlorate cell are made either from mild steel or titanium. The following is the overall reaction in which Me is an alkali metal:

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$$MeCl+3H_2O \rightarrow MeClO_3+3H_2$$

Unlike electrolysis in a chlor-alkali electrolytic cell in which the anode and cathode are separated by a diaphragm or a membrane allowing chlorine and hydrogen

gas produced in the reaction to be evolved and recovered separately, the prior art electrolytic cell for the production of an alkali metal chlorate is not divided into cathode and anode compartments in order to facilitate the reaction of hypochlorous acid and alkali metal hypochlorite to form alkali metal chlorate.

In addition to the principal reaction shown in the equation above, hypochlorite and chlorate are ~~produced~~ REDUCED JRJ 19-JUN-03 mz 6/19/03 at the cathode of the electrolysis cell in an unwanted side reaction. Because of the presence of the highly oxidizing hypochlorite ions in the electrolyte solution, activated cathodes such as the precious metal oxide coated cathodes disclosed in the prior art for use in the production of ~~alkali metal halates~~ CHLOR-ALKALI JRJ 19-JUN-03 mz 6/19/03 cannot be used. Instead, titanium or mild steel cathodes are used in the commercial production of alkali metal chlorate. In chlor-alkali cells, these cathodes require about 450 millivolts and 200 millivolts, respectively, more than precious metal oxide coated cathodes or other activated cathodes. Oxygen-reduction cathodes (also referred to as gas-diffusion or air depolarized cathodes) provide even lower electrical consumption in chlor-alkali electrolytic cells. However, such cathodes have not been useful in an electrolytic cell for the production of alkali metal chlorate because of the presence of hypochlorite ions in the electrolyte.

Millet in '499 discloses conducting an electrolysis process for the production of an alkali metal chlorate without hexavalent chromium values being present in the electrolyte by the electrolysis in an electrolytic cell wherein the anode and cathode are separated by a selectively permeable cationic membrane. Millet describes a process for the preparation of an alkali metal chlorate in a single stage electrolysis reaction in the anode compartment of a "chlorine-soda" cell in which the anode of the cell can be a precious metal oxide coated onto a titanium support and the cathode can be of steel or a precious metal coated onto steel. Since the electrolysis cell is described by Millet as a "chlorine-soda" cell, inherent in such a description is the fact that the membrane selected for use in the cell is necessarily one having 90% to 95% alkali metal ion transport efficiency.

Bommaraju et al. in '951 describe the use of film-coated steel cathodes in an electrolytic cell for the production of an alkali metal halate in order to substantially avoid the presence of hexavalent chromium ions in an alkali metal halite solution. A film-coated, electrically conductive cathode is disclosed to enhance the current efficiency of a cell in which the electrodes are exposed to the same electrolyte. Precious metal oxide coated cathodes for use in the production of alkali metal halates by electrolysis are disclosed by Bommaraju and in U.S. patent No. 4,377,454 and in U.S. patent No. 4,530,742 to Carlin et al. Gas-diffusion cathodes for use in an

electrolytic cell for the electrolysis of brine are disclosed in U.S. patent 5,879,521 to Shimamune et al. and U.S. patent No. 6,080,298 to Andolfatto. In the electrolysis of brine, the gas-diffusion cathodes are disposed in contact with an ion-exchange membrane which partitions the electrolytic cell into anode and cathode compartments.

Wanngard in U.S. patent No. 5,419,818 discloses an electrolysis process for the production of an alkali metal chlorate in a first conventional alkali metal chlorate cell without a separator. The demand for pH-adjusting chemicals is largely avoided by utilization of the acid and alkali metal hydroxide produced in a second electrolytic cell having a cell separator. Preferably, the separator is a cationic-selective membrane which allows the production of concentrated alkali metal hydroxide.

## BRIEF SUMMARY OF THE INVENTION

In the electrolysis process of the invention, electrolytic cells having as a cell separator a low transport efficiency alkali metal ion permselective membrane or an hydrophilic, microporous diaphragm are used for the production of an alkali metal chlorate. In order to provide a process with greater electrical efficiency, the uncatalyzed mild steel or titanium cathodes utilized in commercial, prior art cells for the production of an alkali metal chlorate are replaced in the cells of the invention

with either catalytic, metal cathodes or gas-diffusion cathodes, which are depolarized by feeding air or oxygen to the cathode. To utilize such cathodes without cathode corrosion, the anolyte and catholyte compartments must be separated by a microporous diaphragm or a low transport efficiency alkali metal ion permselective cationic membrane. The electrolysis process of the invention can be carried out with essentially no losses of chlorine, produced in the process, and, in the absence of hexavalent chromium values, derived from the addition of sodium chromate or sodium bichromate to the electrolyte, thus providing economic as well as environmental advantages. The use of a hydrophilic, microporous diaphragm in the electrolysis process of the invention requires that an higher hydraulic pressure be maintained in the catholyte compartment of the cell than in the anolyte compartment of the cell.

The electrolysis process of the invention is advantageous in providing energy savings by (1) reducing the voltage consumption in the electrolysis process, (2) eliminating the addition of chromium ions in the form of hexavalent chromium in the electrolyte with attendant economical and environmental advantages, and (3) MINIMIZING ~~eliminating~~ the need for external sources of hydrochloric acid and sodium hydroxide. Added advantages of the process of the invention include (1) eliminating the possibility of explosive mixtures of oxygen and hydrogen gases and (2) providing an

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electrolysis process for the production of an alkali metal chlorate in which there are essentially no losses of chlorine. The hydrogen produced in the cathode compartment of the cell is confined therein by use of a low transport efficiency alkali metal ion permselective membrane or a hydrophilic, microporous diaphragm thus eliminating contact of hydrogen with the cell anolyte where it can strip away the chlorine produced therein. The anolyte is electrolyzed to a desired solution of an alkali metal halate from which said halate can be directly crystallized.

## BRIEF DESCRIPTION OF THE DRAWING

In the drawing, there is shown a flow sheet for a continuous, cyclic process for the electrolytic production of an alkali metal halate, such as a chlorate, in accordance with one embodiment of the process of the invention. In this process, purified brine enters through line 38 a catholyte recycle stream 40, which exits gas and liquid disengager 19. A catholyte stream comprising alkali metal hydroxide, chlorate, and chloride is removed from catholyte compartment 36 through line 24. Hydrogen is removed from catholyte process stream 24 in gas and liquid disengager 19 and exits through line 17. A catholyte stream overflow from gas and liquid disengager 19 is removed through line 15 and enters anolyte recycle process stream 22 which feeds gas and liquid disengager 18. Chlorine is absorbed from anolyte process stream 22 in gas

and liquid disengager 18 and oxygen is removed through line 20. A final chlorate solution is removed through line 14 from anolyte recycle stream 16 which exits gas and liquid disengager 18. Cell 26 contains an anode 30, a cathode 32, conductive means 31 and 33, and a microporous diaphragm or a low transport efficiency alkali metal ion permselective cationic membrane 28 separating anolyte compartment 34 from catholyte compartment 36. In the preferred process, the pH is maintained in the anolyte compartment 34 at a pH of about 6 to about 7 by measuring and controlling the pH in line 16 at a pH of about 6.8 to about 7.2. Anode 30 is a precious metal oxide coated titanium anode and cathode 32 is either a catalyzed, metal cathode or a gas-diffusion cathode. Where cathode 32 is a gas-diffusion cathode, air or oxygen is fed to one side thereof.

## DETAILED DESCRIPTION OF THE INVENTION

In the process of the invention, an electrolytic cell, preferably, a plate and frame type, containing a low transport efficiency alkali metal ion permselective membrane or an hydrophilic, microporous diaphragm separating the anode and cathode compartments of the cell is used for the preparation of an alkali metal chlorate such as sodium chlorate. The anodes used in the cell of the invention can comprise catalytic, metal anodes such as precious metal oxides deposited on a metal

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substrate such as ~~nickel~~ or titanium. Examples of precious metals used to form the oxides are ruthenium, platinum, and iridium. These anodes have been found to have a high current efficiency in the commercial sodium chlorate electrolytic cell environment at a very low overvoltage for chlorine evolution and operate at close to theoretical current efficiency values. As a result, there is little room for improvement of these prior art catalytic, metal anodes for use in a sodium chlorate electrolytic cell. The cathodes used in the cell of the invention can be gas-diffusion cathodes or catalytic, metal cathodes. For example, precious metal oxides, such as platinum and ruthenium oxides, deposited on a nickel or titanium substrate.

In one embodiment of the process of the invention, low overvoltage precious metal oxide coated cathodes can be used because the cathodes are not exposed to the damaging effect of the hypochlorite ion produced in the anolyte compartment of the cell. In the commercial electrolysis process for producing sodium chlorate, the cathodes of the electrolytic cells are made either from mild steel or titanium. The advantage of mild steel over titanium in the prior art chlorate process is that of lower electrochemical overvoltage and, accordingly, lower electrical power consumption and cost per ton of the sodium chlorate produced. However, mild steel cathodes corrode when the power to the electrolytic cell is shut off for repairs while titanium, which does not corrode when the power is shut off, has a higher overvoltage, thus

consuming more power per ton of chlorate produced. Titanium also forms hydrides during operation of the prior art, commercial electrolytic cells because of the reaction with hydrogen produced at the surface of the cathode. Therefore, in use, the electrode slowly erodes with the formation and subsequent spalling of these titanium hydrides from the surface of the cathode resulting in the necessity for replacement of titanium cathodes periodically at a substantial cost.

In terms of the actual voltages needed for the electrolytic reaction in the process of the invention, the normal reversible potential for the reaction is increased by the values of the electrode potentials and ohmic drops. The increase in the value of the electrode potential over the normal reversible potential for the reaction is termed overvoltage. That is, the difference between the electrode potential necessary for the flow of current and the equilibrium value of the electrode with no current flowing is the overvoltage of the electrode. The overvoltage is related to such factors as the nature of the ion being discharged, the current density, the nature and surface structure of the electrode, the temperature, and the composition of the electrolyte.

A noble metal coated metal substrate as a low overvoltage electrode has been disclosed in U.S. patent No. 4,377,454 to Bommaraju and in U.S. patent No. 3,974,058 to Gokhale. Hydride formation on a titanium cathode has been disclosed as

being effectively prevented by a catalyst coating which is a barrier to the migration of nascent hydrogen. Such cathodes are also disclosed in U.S. patent No. 4,075,070 to DuBois et al. and U.S. patent No. 4,530,742 to Carlin et al. The foregoing patents cited in this paragraph are incorporated herein by reference.

In the process of the invention, non-precious metal oxide coatings on nickel or steel substrates such as mixed oxide electrocatalysts of nickel-molybdenum, nickel-tungsten, cobalt-molybdenum or cobalt-tungsten can be used. These are disclosed in U.S. Patent No. 4,426,269 to Brown et al. Also useful as a catalyzed, metal cathode is an alloy of molybdenum, vanadium, and nickel coating on copper, as disclosed in U.S. Patent No. 4,105,531 to Kuo et al. Also useful as cathodes of the cell and process of the invention are metal alloys such as nickel-iron and nickel-cobalt also containing other transition metals coated onto a nickel or a steel electrode substrate, as disclosed in U.S. Patent No. 4,410,413 to Hall. Also useful as a cathode is a catalyst coating of a mixture of ruthenium metal and ruthenium oxide on a nickel substrate, as disclosed in U.S. Patent No. 5,227,030 to Beaver et al.. The foregoing patents cited in this paragraph are incorporated herein by reference.

Another class of cathodes useful in the cells and process of the invention, which is known to have low overvoltage characteristics in an electrolytic cell for the

production of chlorine and caustic, is an oxygen-reduction cathode, also referred to as a gas-diffusion or air depolarized cathode. Representative gas-diffusion cathodes, disclosed as useful for the electrolysis of brine, are those cathodes disclosed in U.S. patent No. 5,879,521 to Shimamune et al. and U.S. patent No. 6,080,298 to Andolfatto, each incorporated by reference. Where a gas-diffusion cathode is utilized in the electrolysis process of the invention to produce an alkali metal chlorate, the gas-diffusion cathode is placed in the cathode compartment of the electrolysis cell so as to divide the cathode compartment into a solution compartment, on the permselective membrane side and a gas compartment on the opposite side of the gas-diffusion cathode. The gas-diffusion cathode is prepared, for instance, by molding a mixture of a hydrophobic substance such as a polytetrafluoroethylene resin together with a catalyst such that the hydrophobic properties of the cathode prevent liquids from passing through the cathode. Accordingly, when the process of the invention is performed utilizing a gas-diffusion cathode, air or oxygen is fed to a gas compartment, formed on one side of the cathode, which is not shown,.

In one embodiment of the electrolytic process of the invention, every mole of oxidation and reduction that takes place in the electrolytic cell, is accompanied by a mole of ion transport through the cationic permselective membrane. Where sodium is utilized as the alkali metal in the electrolytic production of sodium chlorate, the

sodium ion moves from the anolyte to the catholyte through the permselective membrane. The hydrogen ion can also move from the anolyte compartment to the catholyte compartment. At the same time, water accompanies the transport of these ions from the anolyte to the catholyte. All of the sodium that moves from the anolyte to the catholyte in the form of an ion has to be added back to the anolyte in the form of a sodium hydroxide solution to maintain the pH of the anolyte in the desired range. This constant circulation of sodium from the anolyte to the catholyte as an ion and back to the anolyte as a solution has the effect of keeping the pH of the anolyte at the desired level without any transport of anolyte anions to the cathode compartment. In order to prevent excessive dilution of the anolyte by the addition of a portion of the catholyte, in the process of the invention, that portion of the catholyte which is added to the anolyte to control the pH therein may be concentrated by evaporation of water.

In the process of the invention, permselective cell membranes having low alkali metal ion transport efficiency, generally, less than about 60% of theoretical, preferably, less than about 50% of theoretical, and, most preferably, less than 20% of theoretical are used. The ion transport efficiency of the permselective membrane is expressed as the percentage of the amount of ion transport which actually occurs in comparison with the theoretical amount expected to occur for the measured current flow used. Preferably, said membrane has high hydrogen ion transport efficiency and high water transport efficiency.

The low transport efficiency alkali metal ion permselective membrane must be made of a material which is stable in the cell electrolyte mixture of alkali metal chlorate, hypochlorite and hydroxide solution. The material of the preferred cationic ion exchange membrane can be made of a polymer having cation exchange groups such as carboxylic acid groups and sulfonic acid groups. Suitable polymers include copolymers of vinyl monomers such as tetrafluoroethylene and chlorotrifluoroethylene, and a perfluorovinyl monomer having an ion-exchange group or a reactive group which can be converted into an ion-exchange group.

Alternatively, the permselective membrane of said cell can be replaced by an hydrophilic, microporous diaphragm comprising a polymeric or ceramic material, provided the catholyte compartment of said cell is maintained at a higher hydraulic pressure than the pressure in the anolyte compartment of said cell. Generally, a difference in hydraulic pressure of about 1 to about 48 inches of water, preferably, an hydraulic pressure differential of about 2 to about 24 inches of water, and, most preferably, a catholyte compartment differential pressure of about 4 to about 12 inches of water is used.

Various halogenated polymers are suitable for the formation of the hydrophilic, microporous, diaphragm material useful in the cell and process of the invention.

Examples of useful polymeric diaphragm materials are: fluorinated polymers and fluorinated copolymers such as poly(vinylidene fluoride) and poly(tetrafluoroethylene). Other classes of materials suitable for formation of useful microporous, hydrophilic diaphragms are ceramic materials such as microporous titanium oxide ceramics and microporous zirconia ceramics.

The pore diameter of useful microporous diaphragms can be, generally, about 0.005 to about 1 micron, preferably, about 0.01 to about 0.2 micron, and, most preferably, about 0.05 to about 0.1 micron. The diaphragm thickness usefully can be about 10 microns to about 2 millimeters, preferably, about 25 microns to about 500 microns, and, most preferably, about ~~35~~ 25 microns to about 250 microns. The porosity can usefully be about 50% to about 85%, preferably, about 60% to about 80% and, most preferably, about 65% to about 75%.

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In the process of the invention, caustic from the catholyte is ultimately added to the anolyte in an amount sufficient to control the pH at a desired range of about 6 to about 7. This caustic is not added directly to the anolyte compartment of the electrolytic cell but, rather, at steady state conditions, is added to the anolyte compartment by the addition of said catholyte to an anolyte recycle process stream, as shown in the Figure. This is added to the anolyte as a mixture of caustic and cell feed

brine catholyte solution which overflows from the catholyte compartment to the anolyte compartment. A portion of this catholyte solution also enters the anolyte compartment through the diaphragm where this is used as the cell separator. Control of the pH in the anolyte compartment in the range of 6 to 7 is achieved by measuring the pH in the anolyte recycle stream at a point downstream of the gas and liquid disengager. In the process of the invention, chlorine is absorbed and oxygen is separated. Said recycle process stream enters the anolyte compartment of the cell. The addition of hexavalent chromium to the electrolyte is unnecessary.

In accordance with the process of the invention, the pH of the anolyte of the electrolytic cell is maintained in the range of about 6 to about 7. The anolyte is characterized, for example, as a mixture of sodium chloride and sodium chlorate. This mixture is desirably maintained so as to have a sodium chloride concentration from about 60 grams per liter to about 300 grams per liter and a sodium chlorate concentration from about 60 grams to about 700 grams per liter of the anolyte. The flow rate of anolyte through the cell should be high enough to keep the pH between 6 and 7 as anolyte passes from the bottom to the top of the cell. It has been found that alkali metal chlorate solutions can be made in accordance with the process of the invention at chloride to chlorate mole ratios as low as 0.20. This low ratio is suitable for utilization of the chlorate product as feed in a chlorate crystallizer or the chlorate

solution can be fed directly to a pulp mill chlorine dioxide generator. Further chemical treatment necessary for commercial alkali metal chlorate solutions, such as the removal of hexavalent chromium, is unnecessary.

In the following examples, there are illustrated the various aspects of the invention, but these examples are not intended to limit the scope of the invention. Where not otherwise noted in this specification and claims, temperature is in degrees centigrade and parts or percentages are by weight.

EXAMPLES 1 - 4 (forming no part of this invention)

In order to demonstrate the reduced power usage that can be expected where a precious metal oxide coated cathode is substituted for the titanium or mild steel cathodes presently utilized in commercial sodium chlorate electrolysis cells, a comparison was made of these cathodes as well as an oxygen reduction cathode by measuring the single electrode potential of these cathode materials against a saturated calomel reference electrode. The conditions for measuring the single electrode potentials of these cathode materials were as follows: Sodium hydroxide electrolyte - one molar, current density - one amp per square inch, temperature - 30 to 40 degrees centigrade. Where an oxygen reduction cathode was used, pure oxygen was fed to the

cathode. Cathodes of titanium and mild steel, represent commercial cathodes utilized for the production of sodium chlorate. The precious metal oxide coated cathode was a mixture of platinum and ruthenium oxides thermally deposited on a nickel substrate. The oxygen reduction cathode utilized was a nickel-cobalt-Teflon® mixture thermally deposited upon a sintered nickel substrate.

For a titanium cathode, the measured volts against a saturated calomel reference electrode were found to be -1.55 (-1.07 theoretical).

For a mild steel cathode, the measured volts against a saturated calomel electrode were found to be -1.20 ( -1.07 theoretical).

For a platinum and ruthenium oxide coated nickel substrate cathode, the measured volts against a saturated calomel electrode were -1.08 (-1.07 theoretical).

For the oxygen reduction cathode containing a nickel-cobalt-Teflon mixture thermally deposited on a sintered nickel substrate, the measured volts against a saturated calomel electrode were -0.33 (+0.16 theoretical).

These measured single electrode potentials for these cathode materials can be converted to conventional power usage units of kilowatt hours per short ton of sodium chlorate as follows:

Titanium cathode: 4,800; mild steel cathode: 4,290; platinum and ruthenium oxides coating on nickel: 4,120; and nickel-cobalt-Teflon thermally deposited coating on a sintered nickel substrate: 3,040.

The results above show that mild steel consumes significantly less energy when used as a cathode than titanium, however, mild steel is subject to corrosion in a commercial electrolytic cell for the production of sodium chlorate when the power to the cell is shut off for any reason. Titanium does not corrode under these conditions. But the use of such cathodes in a cell for the production of sodium chlorate results in the consumption of more power per ton of chlorate produced and because titanium forms hydrides during operation of the cell as a result of reaction with hydrogen produced at the surface of the cathode. Thus, a titanium cathode slowly erodes and must be replaced at a substantial cost, as compared to the cost of a cathode of mild steel.

Both precious metal oxide coated cathodes and oxygen reduction cathodes can provide substantially lower power consumption when used in a sodium chlorate electrolytic cell. However, such cathodes are impractical for use in a conventional sodium chlorate electrolytic cell in which the anode and cathode are exposed to the same electrolyte because these cathodes corrode when the power is shut down resulting in contamination of the electrolyte with corrosion products. In addition, the use of an oxygen reduction cathode requires feeding air or oxygen to the cathode and prior art commercial electrolytic cells for the production of sodium chlorate have no means for feeding the required gas to the cathode.

## EXAMPLE 5

A pilot plant size plate and frame type electrolytic cell electrolysis process for the production of sodium chlorate is described in which the anode and cathode compartments are separated by a microporous diaphragm.

The anode used in the cell was a platinum-iridium oxide coated titanium expanded mesh substrate. The activated cathode was a platinum-ruthenium oxide coated nickel expanded mesh substrate. The electrode size was 3 inches by 10 inches providing a total of 30 square inches of active surface area. The microporous

diaphragm utilized to separate the anolyte and catholyte compartments of the cell was a hydrophilic polyvinylidene fluoride sheet sold under the trademark Duropore® by the Millipore Corporation. This diaphragm had a pore diameter of about 0.1 micron, a thickness of 110 plus or minus 30 microns, and a porosity of 70%.

During the operation of the cell, the current input was measured at 35 amps or 1.17 amps per square inch current density. The temperature of both the anolyte and catholyte solutions was maintained at about 65 degrees centigrade by steam heat exchangers. A differential hydraulic pressure of about 4 inches of water from the catholyte compartment to the anolyte compartment was maintained across the diaphragm. During cell operation, purified brine was fed to the cathode compartment of the cell together with a catholyte recycle stream in accordance with the Figure. The brine feed rate to the cathode compartment was 1.52 milliliters per minute. The catholyte was a mixture of sodium hydroxide, sodium chloride, and sodium chlorate. The catholyte was circulated from the top of the cathode compartment, passed through a gas and liquid disengager and returned to the bottom of the cathode compartment. A mixture of sodium chloride and sodium chlorate as anolyte was circulated from the top of the anolyte compartment, passed through a gas and liquid disengager and returned to the bottom of the anode compartment. Both catholyte and

anolyte streams were circulated at a rate of about 2 to about 4 liters per minute. No hexavalent chromium was added to the anolyte or catholyte.

At the beginning of the operation of the cell, the pH of the anolyte compartment was adjusted by the addition of small amounts of hydrochloric acid and sodium hydroxide. After a steady state of pH was achieved, inconsequential amounts of hydrochloric acid and sodium hydroxide were needed to adjust pH over the 40 hour period of operation of the cell. During cell operation, a catholyte overflow stream was removed from the gas and liquid disengager and added to the anolyte recycle stream at a rate of about 1.7 milliliters per minute. An anolyte overflow stream from the anolyte gas and liquid disengager was obtained at a rate of about 1.4 milliliters per minute. During cell operation, at a brine feed rate to the cathode compartment of 1.52 milliliters per minute and utilizing a current of 35 amps, the anolyte reached a concentration of 192 grams per liter of sodium chloride, 260 grams per liter of sodium chlorate, and about 3 to about 5 grams per liter of sodium hypochlorite. During cell operation, a concentration of 48 grams per liter of sodium hydroxide, 198 grams per liter of sodium chloride, and 212 grams per liter of sodium chlorate were obtained in the catholyte. No hypochlorite was detected in the catholyte.

The current efficiency of the cell was measured in two ways: (a) the rate of oxygen evolution can be measured and the current loss calculated as that required to produce oxygen as a by-product and (b) the current efficiency can be measured by analyzing the amount of sodium chlorate made and sodium chloride consumed. The current efficiency of this electrolysis process was 93-94%. The cell voltage averaged 2.74 volts which corresponds to 4,006 kilowatt-hours for the production of each short ton of sodium chlorate produced.

EXAMPLE 6

Example 5 was repeated, except that in the process, using a plate and frame type electrolytic cell, an hydrophilic, polytetrafluoroethylene, microporous diaphragm sold under the trademark Advantec® by Advantec MSF, Inc. was used to separate the anode and cathode compartments of the cell.

The same cathode and anode as those described in Example 5 were used. The diaphragm pore diameter was 0.1 micron, the thickness was 25 plus or minus 1 microns, and the porosity was 71%. The current input was 35 amps or 1.17 amps per square inch current density. The temperature of both the anolyte and catholyte solutions was maintained at about 65 degrees centigrade by steam heat exchangers.

The differential hydraulic pressure from the catholyte to the anolyte compartment was maintained at 4 inches of water.

In the process, purified brine was first acidified to a pH of about 3.5 to remove carbonate ions before being fed, at a rate of about 1.56 milliliters per minute, to the cathode compartment together with a catholyte recycle stream in accordance with the Figure. The cell was run for about 30 hours. During this period, the anolyte concentration was measured at 188 grams per liter of sodium chloride, 245 grams per liter of sodium chlorate, and 3 to 5 grams per liter of sodium hypochlorite. The catholyte concentration was measured at 58 grams per liter of sodium hydroxide, 190 grams per liter of sodium chloride, and 160 grams per liter of sodium chlorate. No hypochlorite was detected in the catholyte. The current efficiency was found to be 93-94%. Chlorine losses were about 0.005% of the current used. This contrasts with commercial electrolytic cells for the production of sodium chlorate which typically exhibit chlorine losses of between 0.3 and 0.5% of the current used. The cell voltage averaged 2.63 volts which corresponds to 3,845 kilowatt-hours for the production of each short ton of sodium chlorate.

EXAMPLES 7 (Control) AND 8

In these examples, the inventive process was compared to a prior art process using two laboratory size electrolytic cells for the preparation of sodium chlorate. In Example 7 a titanium cathode was used and in the second cell of Example 8 an oxygen reduction air depolarized cathode was used. Comparison of the voltage differences between the two cells showed anode to cathode cell voltages of 3.1 to 3.3 volts with the titanium cathode and 1.4 to 2.1 volts with the air depolarized cathode.

Each of the electrolytic cells were plate and frame type cells in which the anode and cathode compartments are separated by a cation exchange membrane made of Nafion® 324, which had a measured sodium ion transport efficiency of 79%. The electrode size was 4 square inches of active area. The current input was 4 amps or 1.0 amp per square inch current density. The air depolarized cathode was a nickel-cobalt sintered nickel cathode. In both cells the anode was a ruthenium and titanium oxide coating on a titanium substrate. The catholyte was maintained at a concentration of sodium hydroxide of 140 to 190 grams per liter. The anolyte concentration of sodium chloride was maintained at 280 to 310 grams per liter. The concentration of sodium chlorate was up to 164 grams per liter. Both anolyte and catholyte liquors were recirculated at the rate of 640 to 660 milliliters per minute and maintained at a

temperature of 70 degrees centigrade. The pH in the anolyte compartment was maintained at 6.2 to 6.7 by the addition of a solution of sodium hydroxide obtained directly from the cathode compartment. It is noted that no hexavalent chromium was added to the anolyte or catholyte.

EXAMPLE 9

In this example, a pilot plant size electrochemical cell for the production of sodium chlorate was run in order to measure the current efficiency, the consumption of hydrochloric acid and sodium hydroxide solution, and the overall cell performance, including the maintenance of a pH of about 6.4 to about 6.8 in an anolyte recycle stream entering the bottom of the anode compartment of the cell. A gas and liquid disengager through which the anode recycle stream passes was used to absorb chlorine to minimize chlorine losses from the system.

The electrolytic cell was similar in components to those of the cell described in Example 8, except that the electrode size was 3.5 inches by 10 inches for a total of 35 square inches of active surface area. The current input was 35 amps or 1.0 amp per square inch current density. The hydrogen evolution cathode was a platinum and iridium oxide coating on a titanium expanded mesh substrate. The anode was a

platinum and iridium oxide coating on a titanium expanded mesh substrate. The catholyte was maintained at a concentration of 140 to 190 grams per liter of sodium hydroxide and the anolyte was a mixture of sodium chloride and sodium chlorate having a concentration of between 188 to 301 grams per liter sodium chloride and 7 to 45 grams per liter sodium chlorate. The anolyte was circulated from the top of the anode compartment to the bottom of the anode compartment in the anolyte recycle stream at a rate of 2 to 4 liters per minute and the temperature of the anolyte and catholyte compartments was maintained at 60 degrees centigrade. No hexavalent chromium was present in the anolyte or catholyte. In the cathode compartment, the agitation of the catholyte by the release of hydrogen at the cathode was sufficient to provide uniform circulation of the catholyte. The pH at the top of the anolyte compartment was controlled by the addition of sodium hydroxide solution, from the cathode compartment, to the anolyte recycle stream and by the adjustment of the flow rate through the anode compartment. The sodium hydroxide solution from the cathode compartment was metered into the anolyte recycle stream as this stream exited at the top of the anolyte compartment of the cell. The addition of caustic at this point in the anolyte recycle stream resulted in a high pH zone in the piping as well as in the disengager located downstream of the caustic addition point. Because of the high pH in this disengager, most of the chlorine, which might otherwise have escaped to the atmosphere in a lower pH anolyte environment, was absorbed from the anolyte.

Subsequently, measuring the pH of the anolyte recycle stream at a point downstream of the disengager allows the maintenance of the anolyte recycle stream in an acceptable pH range by feeding this recycle stream to the bottom of the anolyte compartment of the cell.

The current efficiency of the cell was measured at 96-97% in two ways: (a) by measuring the rate of oxygen evolution from the anode compartment and calculating the current loss required to produce the by-product oxygen and, (b) by analyzing the amount of sodium chlorate made and sodium chloride consumed by the electrolysis current over the test period. Chlorine losses were measured at 0.02% of the current used. It is known in commercial sodium chlorate electrolytic cells that chlorine losses are between 0.3 and 0.5 percent of the current used. The cell voltage averaged 2.86 volts. Sodium ion transport efficiency was measured at 77% and there was a gradual dilution of anolyte salts over the course of the test.

During operation of the cell, no outside sources of hydrochloric acid and sodium hydroxide were utilized. The hydrogen produced at the cathode and the oxygen produced at the anode were not allowed to mix by the use of the permselective membrane separating anolyte and catholyte compartments of the cell. These gases

could be discharged from the cell without mixing and, accordingly, without the formation of explosive mixtures.

EXAMPLE 10

This example is a repeat of Example 9 except that a Nafion 551 permselective membrane was used and the anolyte was a mixture of sodium chloride and sodium chlorate having a concentration of between 70 to 125 grams per liter of sodium chloride and 480 to 593 grams per liter of sodium chlorate. The temperature of the anolyte and catholyte compartments was maintained at 65 degrees centigrade, and the pH in the anolyte was controlled with concentrated, 765 grams per liter, sodium hydroxide solution from an external source.

Under these conditions, the current efficiency of the cell was measured at 92-94%, chlorine losses were measured at 0.35% of the current used, and the cell voltage averaged 2.98 volts. The pH was not controlled as closely as in Example 9 thus resulting in higher chlorine losses. During operation of the cell, no outside sources of hydrochloric acid and sodium hydroxide were utilized. The hydrogen produced at the cathode and the oxygen produced at the anode were not allowed to mix by the use of the permselective membrane separating anolyte and catholyte compartments of the

cell. These gases could be discharged from the cell without mixing and, accordingly, without the formation of explosive mixtures.

Sodium ion transport efficiency of the cell membrane was measured at 65%. By the end of the test, the sodium chloride concentration was 70 grams per liter, the sodium chlorate concentration was 593 grams per liter, and the mole ratio of chloride to chlorate was 0.22. This liquor is suitable for direct feed to a sodium chlorate crystallizer or a pulp mill chlorine dioxide generator with no further treatment.

While this invention has been described with reference to certain specific embodiments, it will be recognized by those skilled in the art that many variations are possible without departing from the spirit and scope of the invention and it will be understood that it is intended to cover all changes and modifications of the invention disclosed herein for the purpose of illustration which do not constitute departure from the spirit and scope of the invention.